California Environmental Protection Agency

Air Resources Board

PROCEDURE FOR THE ANALYSIS OF TOTAL AROMATIC, POLYCYCLIC AROMATIC, AND BIODIESEL CONTENT IN DIESEL FUELS BY SUPERCRITICAL FLUID CHROMATOGRAPHY AND FLAME IONIZATION DETECTOR

Standard Operation Procedure MV-FUEL-160

Version 2.0

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Fuel Analysis and Methods Evaluation Section
Chemical Analysis & Emissions Research Branch
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1   **Introduction**

1   This document describes an automated method for the determination of biodiesel content in diesel fuels by supercritical fluid chromatography. The term "biodiesel" in this standard operating procedure (SOP) refers to Fatty Acid Methyl Esters (FAME) and Fatty Acid Ethyl Esters (FAEE) that can be blended into conventional diesel fuels. Please refer to SOP MV-FUEL-117 for the determination of total aromatic and polycyclic aromatic (PAH) hydrocarbons.

1.2   The range of biodiesel concentrations to which this test method is applicable is from 0 to 40 mass %.

1.3   This procedure is based on a candidate American Society for Testing and Materials (ASTM) test method by Frank DiSanzo (Exxonmobil) and Jody Clark (Selerity Technologies). Alternatively, calculation of the biodiesel content may be based on John Diehl and Frank DiSanzo's 2007 paper, which doesn't require a calibration curve. The same instrument can be used to run ASTM D5186-03(2009) for samples which are known to contain no biodiesel.

2.   **Method**

2.1   The diesel or biodiesel sample is injected onto a packed silica adsorption column and the saturated, monocyclic aromatic and PAH fractions are eluted using supercritical carbon dioxide as the mobile phase, as in ASTM D5186.

2.2   After complete elution of the PAH fractions, the column is back-flushed to allow biodiesel content to elute as a single "total biodiesel" peak.

2.3   The chromatographic areas corresponding to the nonaromatic, monocyclic aromatic, PAH and biodiesel fractions are determined. The biodiesel content is determined using a calibration curve or by normalization. The saturate, monocyclic aromatic, and PAH content are calculated by normalization to (100% - biodiesel content.).

2.4   A flame ionization detector (FID) is used to detect these four groups.

3   **Instrument**

3.1   Supercritical fluid chromatograph (SFC), equipped with SFC Pump, a Liquid Autosampler, a silica column, one or two switching valves, FID, and a computer system running automation software. With two six-way switching valves and an additional column loaded with silver ions for trapping olefins, the instrument can be used also for the olefins analysis using ASTM D6550 without modifications.

4. **Reagents**

4.1   Purity of reagents: Unless otherwise specified, any chemicals used shall be American Chemical Society (ACS) reagent grade or better.

4.2   Carbon dioxide (CO_2), chromatographic grade, 99.995% minimum purity, supplied in a pressurized cylinder equipped with a dip tube.

4.3   Naphthalene, 99+%

4.4   1,2,3,4-tetrahydronaphthalene (tetralin), 99% purity

4.5   Toluene, 99.8%, HPLC grade

4.6   Hexadecane, 99+%, anhydrous

4.7   Zero Air, hydrocarbon free

4.8   Hydrogen, 99.99% minimum purity

4.10   Helium, commercial grade

4.11   Methyl oleate

4.12   Methyl palmitate

5. **Preparation of Instrument**

5.1   Before analysis, the SFC instrument need to be on and warmed up until all the gas flows, the CO2 pressure, the FID, oven and column temperatures are stabilized.

5.2   The cut time t_1 for valve-switching is the same time when the diesel method described in SOP MV-FUEL-117 ends. The back-flush time typically needs to be 1.5 times t_1 or more for the biodiesel content to completely elute.

6. **Calibration**

6.1   The response factor for the biodiesel component is determined using a multipoint calibration curve. The calibration mixtures are blends of equal amounts of methyl oleate and methyl palmitate, diluted with a blend of 75% isooctane and 25% toluene. The total FAME content of the blends are typically 0.5, 10, 20, 30, and 40 mass %. Additional concentration levels may be added.

6.1.1   Calibration curves are generated by the instrument software from analyses of
the calibration mixtures.

6.2   As an alternative to using a calibration curve, the biodiesel fraction can be
calculated by normalization as described in section 9.3 below.

6.3   Detector accuracy, resolution, and retention time repeatability are regularly
checked (see section 10 below) with a performance mixture made up of the
following components, all weighed to the nearest 0.01 g:

> 2 g naphthalene
> 20 g toluene
> 3 g tetralin
> 75 g hexadecane

The naphthalene may take several hours to dissolve completely.

7.   Procedure

7.1   1-2 mL of each sample is transferred into a glass autosampler vial and capped.

7.2   Sample is injected from the vial into the instrument by the autosampler.

7.3   The chromatographic response is integrated by the data system. Results are
calculated as described in section 9.

8.   Safety

8.1   Many of the various components of diesel and biodiesel are toxic and
flammable. Persons using this method must wear protective gloves and
eyewear when working with reagents and samples. Reagents and samples are
used in a fume hood with adequate ventilation.

8.2   All compressed gas cylinders present hazards and should be handled
appropriately. Hydrogen is extremely flammable.

9.   Calculations

9.1   The chromatogram is divided into four sections, each integrated as a single
component.

9.1.1   The first section runs from sample injection to the bottom of the lowest valley
between the retention times of hexadecane and toluene (determined from the
performance mixture analysis, see section 10.1 below.) This area ($Area_1$)
represents the nonaromatic fraction of the sample.

9.1.2   The second section runs from the end of the first section to the beginning of the performance mixture's naphthalene peak (see section 10.1 below). This area ($Area_2$) represents the monocyclic aromatic fraction of the sample.

9.1.3   The third section runs from the end of the second section until the valve-switching. The operator may choose to end the third section earlier to avoid errors due to slight drifts in the baseline. This area ($Area_3$) represents the PAH fraction of the sample.

9.1.4.   The fourth section runs from the beginning of the valve-switching to the end of the chromatogram. Integration starts near twice the valve-switching point of time, and ends when the signal is back to baseline. This area ($Area_{bio}$) represents the biodiesel fraction of the sample.

9.2   The mass % of the biodiesel fraction is calculated by the following equation (automated):

$$C_{bio} = (Area_{bio} - b)/m$$

Where:

C_{bio} (%) = Concentration of biodiesel, mass%
$Area_{bio}$ = area of biodiesel 'peak'
m = slope of the linear least squares regression line from the calibration curve
b = intercept of the linear least squares regression line from the calibration curve

9.3   Alternatively, without a calibration curve, a response factor (RF) of 1.19 may be used for the biodiesel fraction, while a RF of 1 is used for the other three sections of the chromatogram. Therefore, the mass % of the biodiesel fraction may be calculated by the following equation (automated):

$$C_{bio} = (1.19 \times Area_{bio}) / (Area_1 + Area_2 + Area_3 + 1.19 \times Area_{bio})$$

10   **Quality Control**

10.1   The performance mixture described in section 6.2 above is analyzed twice at the beginning of the analysis day, once after every ten samples, and once again at the end of the analysis day. The analyses serve four functions:

10.1.1   Detector resolution is checked with every performance mixture analysis according to the following equations:

$$R_{NM} = \frac{2 \times (t_2 - t_1)}{1.699 \times (y_2 + y_1)}$$

$$R_{MP} = \frac{2 \times (t_4 - t_3)}{1.699 \times (y_4 + y_3)}$$

Where: R_{NM} = resolution between the nonaromatic and monoaromatic peaks
R_{MP} = resolution between the monoaromatic and polycyclic aromatic peaks
t_1 = time (seconds) for the n-C_{16} peak apex
t_2 = time (seconds) for the toluene peak apex
t_3 = time (seconds) for the tetralin peak apex
t_4 = time (seconds) for the naphthalene peak apex
y_1 = peak width at half height (seconds) of the hexadecane peak
y_2 = peak width at half height (seconds) of the toluene peak
y_3 = peak width at half height (seconds) of the tetralin peak
y_4 = peak width at half height (seconds) of the naphthalene peak

R_{NM} must be at least four and R_{MP} must be at least two in order for the detector to pass the resolution test.

10.1.2   Retention time repeatability is checked using the initial two performance mixture analyses of the day. The retention times of hexadecane and toluene must not differ by more than 0.5% between the two runs.

10.1.3   Detector accuracy is checked with every performance mixture analysis. For each component of the performance mixture, a relative response factor is determined from the chromatogram according to the following equations:

$$RF_i = \frac{A_i}{M_i}$$

$$RRF_i = \frac{RF_i}{RF_{C16}}$$

where

A_i =   Area % of component I in the performance mixture
M_i =   Known mass % of component I in the performance mixture
RF_i=   Response Factor of component I
RF_{C16} =   Response Factor of hexadecane in the performance mixture
RRF_i =   Relative Response Factor of component I

These empirical relative response factors are compared with theoretical relative response factors calculated by the following equations:

$$RRF_{theor} = \frac{(12.01n)}{MW} \times \frac{(226.4)}{12.01 \times 16}$$

where:

> 12.01 = the atomic mass of carbon
> n = the number of carbon atoms in the component molecule
> MW = molecular mass of the component molecule
> 226.4 = molecular mass of hexadecane
> 16 = the number of carbon atoms in hexadecane

The measured RRF_i for each component (toluene, tetralin and naphthalene) in the test mixture must be within 10% of the theoretical value as calculated with the above equation or summarized in Table 1.

Table 1: Theoretical Response Factors

Component	Carbons	Molecular Mass	RRF(Theor)
Toluene	7	92.13	1.075
Tetralin	10	132.2	1.070
Naphthalene	10	128.2	1.104

10.1.4 The beginning time of the naphthalene peak is determined for every performance mixture analysis. This time is used in calculating results for the next set of samples (see sections 9.1.1 through 9.1.3 above.)

10.2 If any of the tests in section 10.1 above result in a failure, appropriate corrective action must be taken and the performance mixture rerun before any more samples may be analyzed.

10.3 Pure hexadecane is run as a blank once during each analysis day. If the total aromatics result is greater than 0.5 mass % or the PAH result is greater than 0.2 mass %, corrective action must be taken.

10.4 Repeatability and Reproducibility are not established for this method. As a result, no replicate is required.

11 References

11.1   Standard Test Method for Determination of Total Biodiesel Fatty Acid Methyl (FAME) and Hydrocarbon Types in Diesel Fuels by Supercritical Fluid Chromatography, Subcommittee D02.04 on Hydrocarbon Analysis, ASTM International (method number not yet assigned.)

11.2   J.W. Diehl and F. P. DiSanzo, Determination of Total Biodiesel Fatty Acid Methyl, Ethyl Esters and Hydrocarbon Types in Diesel Fuels by Supercritical Fluid Chromatography/ Flame Ionization Detection, Journal of Chromatographic Science, Vol. 45, pages 690-693, 2007.

12 Revision History

Version 1.0:   Effective date: February 1, 2016

Version 2.0:   Effective date: May 1, 2017.

Significant Changes:

Deleted references to all SFC vendors.